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Different Hydrodynamic Model for Gas-Phase Propylene Polymerization in a Catalytic Fluidized Bed Reactor

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***Abstract*— A comparative simulation study was carried out using the improved well-mixed, constant bubble size and well mixed models. These fluidized bed reactor models, combined with comprehensive kinetics for propylene homo-polymerization in the presence of a multiple active site Ziegler-Natta catalyst. In the improved model, the effect of the presence of particles in the bubbles and the excess gas in the emulsion phase was taken into account to improve the quantitative understanding of the actual fluidized bed process. The superficial gas velocity and catalyst feed rate have a strong effect on the hydrodynamics and reaction rate, which results in a greater variation in the polymer production rate and reactor temperature. At typical operating conditions the improved well mixed and well mixed models were in good agreement. While the constant bubble size model was found to over-predict the emulsion phase temperature and under-predict propylene concentration.**

Keywords-component; hydrodynamics; fluidized bed reactor; propylene polymerization; Ziegler-Natta catalyst

I. INTRODUCTION

Advantages of fluidized bed reactors (FBR) such as their ability to carry out a variety of multiphase chemical reactions, good particle mixing, high rate of mass and heat transfer and their ability to operate in continuous state has made it one of the most widely used reactor for polyolefin production . Consequently, considerable attention has been paid to model propylene polymerization in fluidized bed reactors.

In heterogeneous systems, polymerization occurs in the presence of different phases with inter-phase mass and heat transfer and chemical reaction. Phenomena such as complex flow of gas and solids, kinetics of heterogeneous polymerization and various heat and mass transfer mechanisms must be incorporated in a realistic modeling approach. Several different methods for describing the hydrodynamics of the fluidized bed polyolefin reactor have been proposed in literature. McAuley et al. [1] considered the fluidized bed polyolefin reactor as a well mixed reactor. They compared the simple two-phase and the well mixed models at steady state conditions and showed that the well mixed model does not exhibit significant error in the prediction of the temperature and monomer concentration in the reactor as compared with the simple two-phase model at steady state conditions. Choi and Ray [2] presented a simple two-phase model in which the reactor consists of emulsion and bubble phases. They assumed that the polymerization reaction occurs only in the emulsion since the bubbles are solid-free. Hatzantonis et al. [3] considered that the reactor comprises a perfectly mixed emulsion phase and a bubble phase divide into several solid-free well-mixed compartments in series. Alizadeh et al. [4] proposed a tanks- in-series model to represent the hydrodynamics of the reactor.

In the present study, previous works on the modeling of gas-phase olefin polymerization fluidized-bed reactors were extended to account for the dynamic behavior of propylene polymerization in fluidized bed reactors.

II. POLYMERIZATION MECHANISM AND KINETIC MODEL

The single-site kinetic model is not capable of describing the kinetic behavior, production rate and molecular weight distribution of propylene homo-polymerization. Therefore, a two-type active site was considered in the present study.

Each site type is associated with different rate constant for formation, initiation, propagation and chain transfer. For details of the polymerization reactions and kinetic model, the reader is referred to a paper by Shamiri et al. [5].

The reaction rate constants were taken from similar reactive system [5, 6]. The rate constants are given in Table 1.

III. SIMPLIFIED HYDRODYNAMIC MODELS

McAuley et al. [1, 7] proposed a simplified well-mixed model by assuming that bubbles are very small or unrestricted mass and heat transfer between the bubble and emulsion phases and the temperature and composition are uniform in the gas phase throughout the bed.

The simple two-phase flow structure for the gas-phase olefin polymerization model has been used previously in the literature [1-3]. This model assumes the existence of solid-free bubbles in the fluidized bed while the emulsion remains at minimum fluidization conditions. For details of the well mixed and simple two phase flow structure

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(Constant bubble size) models, the reader is referred to a paper by Hatzantonis et al. [3].

IV. IMPROVED HYDRODYNAMIC MODELS

The conventional constant bubble size and well mixed models assume that the emulsion is at minimum fluidization ($\varepsilon_e = \varepsilon_{mf}$) and bubbles are solid-free ($\varepsilon_b = 1$). This theory is not able to predict the effect of the dynamic gas–solid distribution on the apparent reaction and heat/mass transfer rate in the fluidized beds properly and is limited to explain the low-velocity bubbling fluidization However, the existence of solid particles in the bubbles has been proved both experimentally and theoretically [8]. The emulsion also does not remain at minimum fluidization conditions and it may contain more gas at higher gas velocities [8, 9]. A better mixing of the two phases which results in more solid particles entering the bubbles and more gas entering the emulsion phase occurs while the superficial gas velocity increases in a fluidized bed. In the present study, the dynamic two-phase model was used to improve the quantitative understanding of the actual process.

A. Improved well mixed model

In this model, it is assumed that there are negligible mass and heat transfer resistances between the emulsion gas and solid polymer particles as well as that between the bubble and emulsion phases. Therefore, a pseudo-homogeneous single-phase model could be used. Based on the model assumptions and the improved hydrodynamic model as described above, the following dynamic material and energy balance with hydrodynamic equations can be written for all of the compositions in the bed. Monomer and hydrogen dynamic molar balance is written as:

$$(AH\varepsilon_{ave})\frac{d[M_i]}{dt} = U_e A([M_i]_{in} - [M_i]) - R_v \varepsilon_{ave}[M_i] - (1-\varepsilon_{ave})R_i \tag{1}$$

The dynamic energy balance is given by:

$$\left[\sum_{i=1}^{m}[M_i]C_{pi}AH\varepsilon_{ave} + AH(1-\varepsilon_{ave})\rho_{pol}C_{p,pol}\right]\frac{dT}{dt} = U_e A\sum_{i=1}^{m}[M_i]C_{pi}(T_{in}-T_{ref}) - U_e A\sum_{i=1}^{m}[M_i]C_{pi}(T-T_{ref}) - R_v\left[\sum_{i=1}^{m}\varepsilon_{ave}[M_i]C_{pi} + (1-\varepsilon_{ave})\rho_{pol}C_{p,pol}\right](T-T_{ref}) + (1-\varepsilon_{ave})\Delta H_R R_p \tag{2}$$

The correlations required to evaluate the average bed voidage from dynamic two-phase flow structure model are as follows [8, 9]:

$$\delta = 0.534\left[1-\exp\left(-\frac{U_0-U_{mf}}{0.413}\right)\right] \tag{3}$$

$$\varepsilon_e = \varepsilon_{mf} + 0.2 - 0.059\exp\left(-\frac{U_0-U_{mf}}{0.429}\right) \tag{4}$$

$$\varepsilon_b = 1 - 0.146\exp\left(-\frac{U_0-U_{mf}}{4.439}\right) \tag{5}$$

$$\varepsilon_{ave} = (1-\delta)\varepsilon_e + \delta\varepsilon_b \tag{6}$$

$$V_p = Ah(1-\varepsilon_{ave}) \tag{7}$$

The dynamic monomer internal energy is considered to be negligible in the energy balance equation. The initial conditions for the solution of model equations are as follows:

$$[M_i]_{t=o} = [M_i]_{in} \tag{8}$$

$$T(t=0) = T_{in} \tag{9}$$

V. RESULTS AND DISCUSSION

In order to demonstrate the predictive capabilities of the proposed different hydrodynamic sub-models along with the reaction sub-model, simulations were carried out at the operating conditions shown in Table 2.

A. Effect of catalyst feed rate

The molar flow rate of potential active sites into the reactor is proportional to the mass feed rate of the catalyst. This makes the later an important operating parameter in polypropylene fluidized bed reactors. Fig. 1 shows the effect of catalyst feed rate on the polypropylene production rate. It is clear that the polymer production rate is directly proportional to the catalyst feed rate. As the catalyst feed rate increases, so does the polymer production rate. This is due to the increase in the available reaction sites. The improved model shows lower production rate compared to the conventional well mixed and constant bubble size models since it predicts higher void fraction of the bed. Fig. 3 illustrates the effect of step changes in the catalyst feed rate on the dynamic behavior of the three models in terms of emulsion phase temperature. The initial catalyst feed rate was assumed to be 0.3 g/s. when the emulsion phase temperature reached steady state, the catalyst feed rate was changed by ±0.1 g/s. As can be seen in Fig. 2, the catalyst feed rate strongly affects the emulsion phase temperature and a small step change in the catalyst feed rate changes the temperature of the reactor. Emulsion temperature predicted by the improved well mixed model is lie between the temperatures predicted by the other two models and shows intermediate behavior. The constant bubble size model shows a higher deviation. It should be pointed out that when the catalyst feed rate is changed from 0.3 g/s to 0.4 g/s, the constant bubble size model predicts a temperature above the accepted industrial safety limit of 80 °C [10]. Working above this critical temperature may lead to particle agglomeration problems.

B. Effect of superficial gas velocities

The superficial gas velocity is directly related to the monomer residence time in the reactor, heat removal rate from the reactor and fluidization conditions. Effect of superficial gas velocity on the polymer production rate predicted by various models is illustrated in Fig. 3. This figure illustrates that, all three models predict that the polymer production rate decreases by increasing the superficial gas velocity. In fact, increasing the superficial gas velocity decreases the monomer residence time which leads to decreasing the monomer conversion and polymer production rate. The production rate predicted by the improved model is less than the conventional models since based on the improved hydrodynamic correlations, an increase in the superficial gas velocity increases the average bed void fraction and emulsion phase velocity which leads to reducing the volume of solids in the reactor. Therefore, the monomer mean residence time is reduced, resulting in decreasing the total monomer conversion and polymer production rate compared to the conventional models.

VI. CONCLUSIONS

An improved dynamic model for the production of polypropylene in a gas phase fluidized bed reactor was developed to describe the hydrodynamics of the fluidized bed reactor of polypropylene production was based on the dynamic two-phase concept of fluidization. Comparative simulation studies were carried out using the well-mixed, constant bubble size model and the improved well mixed models in order to investigate the effects of the mixing, operating conditions, kinetic and hydrodynamic parameters on the reactor performance. The improved model showed different prediction characteristics of polymer production rate as well as heat and mass transfer behavior as compared to other published models. The constant bubble size model was found to over-predict the emulsion phase temperature and under-predict propylene concentration. All the three models showed similar dynamic behavior at the startup conditions. Furthermore, the improved well mixed model predicted a narrower safe operation window. The superficial gas velocity and catalyst feed rate have a strong effect on the hydrodynamics and reaction rate which results in a greater variation in the total production rate.

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TABLE 2 REACTIONS RATE CONSTANTS

Reaction	Rate constant	Unit	Site Type 1	Site Type 2	Reference
Formation	$K_f(j)$	s^{-1}	1	1	[5]
Initiation	$K_i(j)$	$lmol^{-1}s^{-1}$	22.88	54.93	[6]
	$K_h(j)$	$lmol^{-1}s^{-1}$	0.1	0.1	[5]
	K_{hr}	$lmol^{-1}s^{-1}$	20	20	[5]
Propagation	$K_p(j)$	$lmol^{-1}s^{-1}$	208.6	22.8849	[6]
Activation energy		$kcalmol^{-1}$	7.2	7.2	
Transfer	$K_h(j)$	$lmol^{-1}$	0.0462	0.2535	[6]

	$K_{fm}(j)$	$lmol^{-1}$	7.54	7.54	[6]
	$K_{fh}(j)$	$lmol^{-1}$	0.12	0.12	[5]
	$K_{fr}(j)$	$lmol^{-1}$	0.0001	0.0001	[5]
Deactivation	$K_{ds}(j)$	s^{-1}	0.00034	0.00034	[6]
	$K_{di}(j)$	$lmol^{-1}s^{-1}$	2000	2000	[5]

TABLE 2 OPERATING CONDITIONS AND PHYSICAL PARAMETERS CONSIDERED IN THIS WORK FOR MODELING FLUIDIZED BED POLYPROPYLENE REACTORS

Operating conditions	Physical properties
V (m^3)=50	μ (Pa.s)=1.14×10-4
T_{ref} (K)=353.15	ρ_g (kg/m^3)=23.45
T_{in} (K)=317.15	ρ_s (kg/m^3)=910
P (bar)=25	dp (m) =500×10^{-6}
Propylene concentration (mol/lit)=1	ε_{mf}=0.45
Hydrogen concentration (mol/lit)== 0.015	
Catalyst feed rate (g/s)= 0.2	

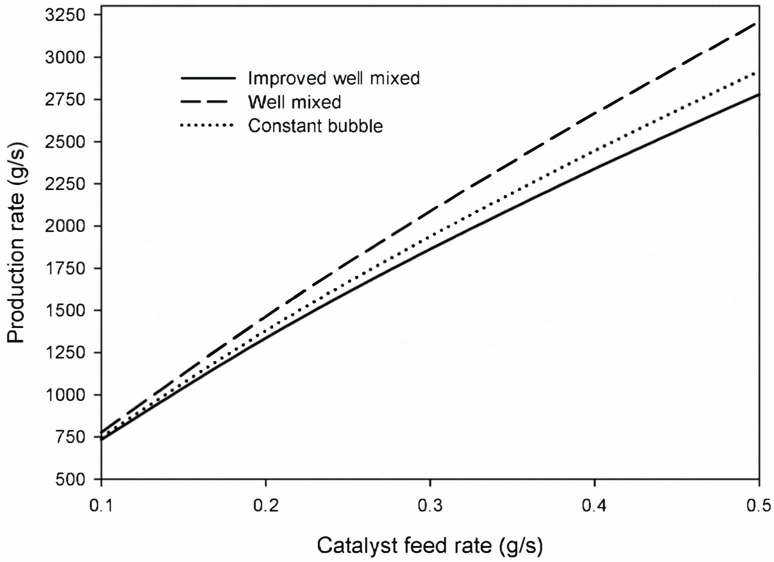

Fig. 1. Effect of catalyst feed rate on polymer production rate at U_0=0.35 m/s.

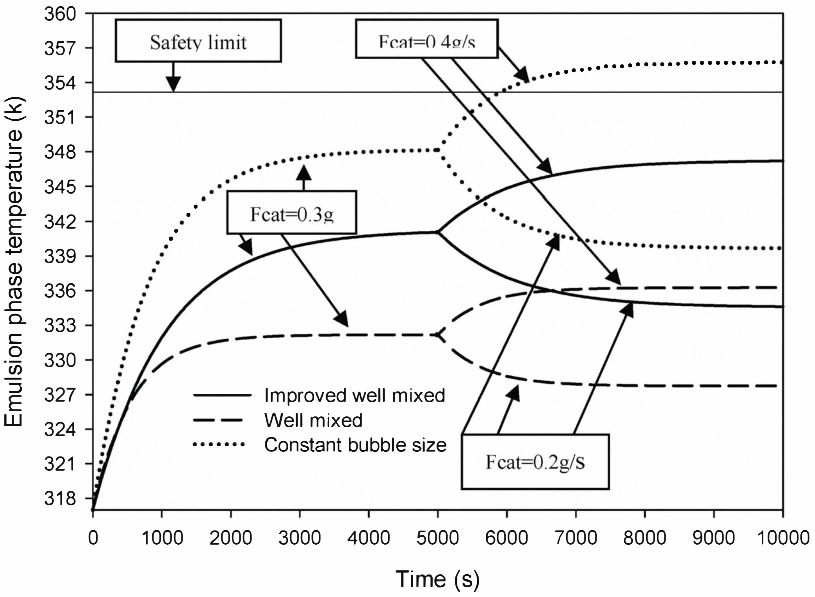

Fig. 2. Effect of step change in the catalyst feed rate from 0.3 g/s to 0.2 or 0.4 g/s on the emulsion phase temperature calculated by the three models at U_0=0.35 m/s.

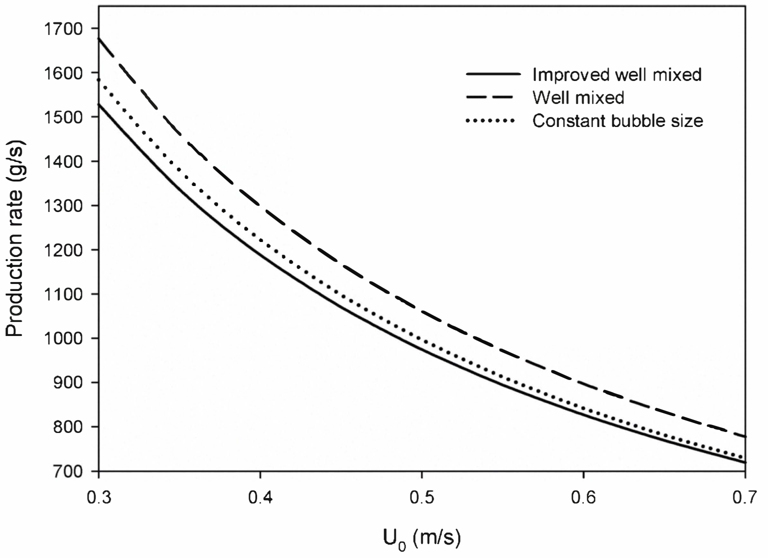

Fig. 3. Effect of superficial gas velocity on the product rate at Fcat=0.2 g/s.